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Adsorption of Pollutants from Complex Offset Printing Wastewaters: Mechanisms, Mass Transport and Kinetic Models

ABSTRACT

This paper presents an overview of the theoretical basis of liquid–solid adsorption, with an emphasis on physical and chemical adsorption, the main stages of mass transport and the most frequently applied kinetic models. Particular attention is paid to the limitations of interpreting kinetic data and to the distinction between mathematical fitting and the actual adsorption mechanism. The overview indicates that reliable interpretation of adsorption processes must consider both surface interactions and mass-transfer resistances in the boundary layer and in adsorbent pores. In the context of printing engineering, these theoretical considerations are particularly relevant for the treatment of offset printing effluents such as waste developer and waste fountain solution, where adsorption is used as a polishing step following electrocoagulation/flotation as the primary treatment stage.

KEY WORDS
Adsorption, mass transport, adsorption kinetics, offset printing effluents

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1. Introduction

Industrial development is inevitably accompanied by the generation of wastewaters of complex composition containing organic and inorganic pollutants of different origins and reactivities. The selection of an appropriate treatment method depends on the effluent composition, pollutant concentration, process requirements and economic constraints. Among the available treatment methods, adsorption occupies a prominent place because of its ease of implementation, chemical stability of adsorbents, high affinity towards dissolved substances and high removal efficiency at low pollutant concentrations (Deryło-Marczewska et al., 2010; Sen Gupta & Bhattacharyya, 2011). These characteristics make adsorption particularly suitable for polishing stages in complex printing wastewater treatment trains, where stringent discharge limits must be met despite variable effluent composition.

The importance of adsorption is especially pronounced in complex industrial wastewaters, where a high total organic load is accompanied by competitive effects of different dissolved species. In such systems, successful application of adsorption treatment depends not only on adsorption capacity, but also on the adsorption mechanism and process kinetics. Therefore, understanding mass transport and the proper interpretation of kinetic models are essential for the design and optimisation of adsorption systems and for minimising operating costs in industrial practice (Qiu et al., 2009; Ponnusami et al., 2010; Sen Gupta & Bhattacharyya, 2011).

Within the context of wastewater management in the printing industry, this issue is particularly important for offset printing effluents, since waste offset developer and waste fountain solution contain complex mixtures of dissolved organic substances and require carefully selected treatment sequences. Theoretical understanding of adsorption therefore has direct practical value for the design of combined electrocoagulation/flotation and adsorption treatment systems in printing practice.

2. Mechanisms of adsorption and mass transport

Adsorption is defined as a change in the concentration of a component at the interface between two phases, and in a liquid–solid system the adsorbate is transferred from the solution and bound to the surface of a solid adsorbent. Depending on the nature of the bonds established between the adsorbent and the adsorbate, two limiting forms of adsorption are distinguished: physical adsorption and chemical adsorption, which represent two extremes of a continuum of possible interaction mechanisms (Adamović, 2016).

Physical adsorption is based on van der Waals forces, London forces and dipole–dipole interactions, is generally reversible and occurs with lower adsorption enthalpies. In contrast, chemical adsorption involves stronger ionic, covalent, coordinate covalent or hydrogen bonds, is usually irreversible and is associated with higher adsorption enthalpies. Physical adsorption often results in multilayer adsorption, whereas chemical adsorption is usually associated with monolayer formation at active sites on the adsorbent surface (Tričković, 2009; Kostić, 2014).

In real systems, physical and chemical adsorption need not be strictly separated and may occur simultaneously or successively. Therefore, the adsorption mechanism cannot be interpreted solely on the basis of assumed bond type, but must be linked to process kinetics and transport limitations within the system (Qiu et al., 2009; Sen Gupta & Bhattacharyya, 2011).

Mass transport of dissolved adsorbate species from the bulk solution to the active sites of the adsorbent is an integral part of every adsorption process. When the adsorbent is porous, the transport mechanism may be described through four stages: bulk diffusion through the solution, film diffusion through the hydrodynamic boundary layer, intraparticle diffusion through the pores of the adsorbent and, finally, adsorption by binding of adsorbate molecules to active sites inside the pores (Kuo et al., 2008; Wang et al., 2008; Doğan et al., 2009; Çeçen & Aktaş, 2011).

Some authors describe liquid–solid adsorption through three basic steps: transport of the adsorbate from the liquid phase to the external surface of the adsorbent, transport through the liquid film attached to the adsorbent surface and interaction of the adsorbate with active sites on the adsorbent surface leading to physical or chemical adsorption (Hameed & El-Khaiary, 2008; Plazinski et al., 2009; Valderrama et al., 2010; Sen Gupta & Bhattacharyya, 2011). Regardless of whether a three-step or four-step representation is used, the essential point remains the same: the slowest step determines the overall process rate.

If the slowest step is transport through the solution or the boundary layer, adsorption can be regarded as transport-controlled. When intraparticle diffusion is the slowest step, pore structure and particle size become decisive factors. Only when the interaction of the adsorbate with active sites is the slowest stage can adsorption be considered chemically controlled. Transport-controlled adsorption is more common at low mixing intensity and low adsorbate concentration, whereas under intensive mixing, higher adsorbate concentration and with porous adsorbents of small particle size, intraparticle diffusion may become dominant (Wang et al., 2008; Plazinski et al., 2009; Ahmaruzzaman, 2010; Sen Gupta & Bhattacharyya, 2011).

For offset printing effluents, such distinctions are important because the composition of treated developer or fountain solution may include a broad spectrum of organic compounds with different diffusivities and affinities for activated carbon or carbon nanomaterials. Consequently, the same adsorbent may exhibit different apparent kinetic behaviour depending on the wastewater matrix and pretreatment stage. As a result, appropriate kinetic modelling becomes essential for quantifying mass-transport limitations and identifying the dominant adsorption mechanism in such complex systems.

3. Adsorption kinetic models

In the design of adsorption treatment, the most important parameters for characterizing adsorbents are adsorption capacity and adsorption kinetics. Kinetic analysis provides information on the rate of attainment of equilibrium, the possible adsorption mechanism, the transition states within the system and the suitability of a given adsorbent for technological and environmental applications, including printing wastewater treatment (Deryło-Marczewska et al., 2010; Sen Gupta & Bhattacharyya, 2011). Mathematical models used for the analysis of adsorption data may generally be divided into reaction models and diffusion models. Reaction models describe the change of adsorption capacity with time without explicit consideration of mass transport, whereas diffusion models attempt to represent the

actual course of adsorption through film diffusion, intraparticle diffusion and mass transfer to active sites in the adsorbent (Qiu et al., 2009; Ponnusami et al., 2010).

3.1. Lagergren's pseudo-first-order model

Lagergren's pseudo-first-order model is among the oldest and most frequently used models for the description of adsorption kinetics in liquid–solid systems. It assumes that the adsorption rate is proportional to the difference between the equilibrium adsorption capacity and the capacity at a given time (Wang et al., 2008; Qiu et al., 2009).

The applicability of this model strongly depends on the reliable determination of the equilibrium adsorption capacity. In practice, the pseudo-first-order model is often suitable only for the initial period of adsorption, whereas at longer contact times significant deviations may appear between experimental and theoretically calculated values. Therefore, its interpretation must be approached with caution, especially when the aim is to infer the nature of the adsorption mechanism from mathematical fitting alone (Aly et al., 2014).

3.2. Pseudo-second-order model

The pseudo-second-order model assumes that the adsorption rate depends on the number of unoccupied active sites and is frequently associated with chemical interaction between the adsorbate and the adsorbent. In a large number of adsorption systems, this model shows very good agreement with experimental data, especially for the adsorption of organic and inorganic pollutants on carbonaceous adsorbents (Hameed, 2008; Sen Gupta & Bhattacharyya, 2011; Aly & Luca, 2013; Plazinski, 2013).

However, good agreement with the pseudo-second-order model does not necessarily mean that the process is exclusively chemically controlled. The literature indicates that the same model may also be successfully applied to systems where physical adsorption and diffusion resistances play an important role. Therefore, the pseudo-second-order model may be regarded as a useful mathematical description of adsorption kinetics, but not as sufficient proof for the unequivocal definition of the adsorption mechanism (Plazinski et al., 2009; Qiu et al., 2009).

3.3. Elovich model

The Elovich model was developed for chemisorption processes on energetically heterogeneous surfaces. Its basic assumption is that the adsorption rate decreases exponentially with the increasing amount adsorbed, while desorption and interactions between adsorbed species do not have a dominant effect at low surface coverage (Plazinski et al., 2009; Sen Gupta & Bhattacharyya, 2011).

This model is applied to describe the adsorption of various pollutants, including phosphates, cadmium, chromium, copper, phenols, and nitroaromatic compounds. Its advantage lies in accounting for the energetic heterogeneity of the adsorbent surface, but even good agreement with the Elovich model is not sufficient for an independent interpretation of the overall adsorption mechanism without complementary mass-transfer analysis (Qiu et al., 2009; Shen et al., 2009; Sheng et al., 2010).

3.4. Diffusion models

Unlike reaction models, diffusion models aim to describe the actual course of adsorption through successive mass-transport steps. In practice, the Weber–Morris intraparticle diffusion model and the Dumwald–Wagner model are most commonly used. The Weber–Morris model is based on the dependence of the adsorbed amount on the square root of time and is used to estimate the contribution of intraparticle diffusion to the overall adsorption kinetics. If the linear portion of the plot passes through the origin, intraparticle diffusion may be considered the sole rate-controlling step over the corresponding adsorption stage. Deviation from the origin indicates the presence of additional resistances, most often film diffusion (Alkan et al., 2007; Hameed, 2008; Doğan et al., 2009; Valderrama et al., 2010).

The Dumwald–Wagner model is also used to analyse internal diffusion and to assess whether intraparticle transport is the determining step of the adsorption process. The advantage of diffusion models is that they offer a more realistic insight into the adsorption pathway than reaction models, especially in systems with porous adsorbents and pronounced transport resistances. Therefore, their use should be an integral part of any serious kinetic analysis of adsorption systems (Cheng et al., 2008; Qiu et al., 2009; Hai et al., 2012; Tang et al., 2012).

A practical implication for wastewater treatment in the printing industry is that reactor design based only on pseudo-second-order fitting may lead to suboptimal contact times and adsorbent doses. For real offset printing effluents, diffusion analysis is needed in order to distinguish between surface interaction effects and matrix-dependent transport limitations and to avoid misleading mechanistic conclusions based solely on reaction-model fitting.

4. Discussion

The literature overview shows that pseudo-first-order and pseudo-second-order models are very frequently used in adsorption studies, whereas diffusion models are

usually applied as complementary tools for mechanism interpretation. However, reaction models alone cannot represent the real adsorption pathway because they do not explicitly include mass transport stages. As a result, they often provide a good mathematical fit to experimental data, but without sufficient basis for an unambiguous conclusion about the dominant mechanism of the process (Qiu et al., 2009; Ponnusami et al., 2010).

Proper interpretation of adsorption kinetics requires simultaneous consideration of the properties of the adsorbent and adsorbate, mixing conditions, adsorbate concentration, particle size and porosity of the adsorbent, as well as the results obtained from both reaction and diffusion models. Only such an approach allows a more reliable distinction between transport-controlled and chemically controlled adsorption. In this sense, kinetic analysis should not be regarded as a formal approximation of experimental data, but rather as an important tool for the rational design of adsorption treatments for complex industrial wastewaters (Ahmaruzzaman, 2010; Sen Gupta & Bhattacharyya, 2011).

The relevance of this theoretical framework lies in its direct applicability to the optimisation of wastewater treatment in offset printing production systems. Adsorption can serve as a polishing stage after electrocoagulation/flotation treatment of offset printing effluents, while the correct interpretation of kinetic models helps prevent oversimplified conclusions during process scale-up and practical implementation.

5. Conclusion

Adsorption is an efficient and flexible method for the removal of organic matter from complex industrial wastewaters. The apparent adsorption rate and the observed kinetic behaviour are determined by the combined influence of adsorbate–adsorbent surface interactions and mass-transfer resistances, with the slowest stage controlling the overall process kinetics. Lagergren's pseudo-first-order model, the pseudo-second-order model and the Elovich model are useful for the mathematical description of kinetics, whereas diffusion models allow a more realistic assessment of the adsorption pathway and identification of the dominant transport limitations. Therefore, reliable interpretation of adsorption mechanisms can only be achieved through the combined use of reaction and diffusion models together with critical consideration of the experimental conditions (Qiu et al., 2009; Sen Gupta & Bhattacharyya, 2011).

In addition, for wastewater streams generated in offset printing, the combination of adsorption theory with application-specific knowledge can support the development of more efficient and better-supported treatment strategies for waste offset developer and waste fountain solution in combined electrocoagulation/flotation–adsorption treatment trains. The conceptual framework discussed in this paper is also relevant for the treatment of effluents from other printing techniques and, more broadly, for adsorption-based polishing stages in wastewater management across the printing industry.

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